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(54) Title: LUMINESCENT LATEX MIXTURE AND PRODUCTS

(57) Abstract: The invention offers the balloon industry (in particular) a solution to the problem that coagulation of latex is inhibited by improved luminescent phosphors such as strontium aluminate. Phosphor particles are coated in a resin or wax or the like, substantially impervious to water. Various formulations, including inks and paints, and several procedures for the manufacture of articles involving those compounds are also provided. Highly luminous balloons and other latex-based articles optionally decorated by printing or embossing techniques may be made.

TITLE Luminescent latex mixture and products

FIELD

This invention relates to compositions including luminescent strontium-aluminate phosphors plus materials such as latex, and in particular to items comprised at least in part of a latex mixture of this type, such as inks, paints, containers, balloons, condoms, or the like.

BACKGROUND

There is often a desire to enhance the visual appearance of an object by including some form of light-generative capability within it. This can also be useful. Luminescence, by which we mean the ability of a substance to evolve light over a period following an exposure of the material to light generally of a shorter wavelength, can be distinguished from fluorescent materials by the duration of the afterglow, the evolution of "stored" light. Zinc sulphide based luminescent materials have been known for many years. Recently invented types of phosphorescent material involve alkaline earth metal aluminates such as strontium aluminate (Lange, US 3294699, UK patent 1190520, Japanese patent (1994) JP 000268463, or US 5885483 to Hao, Q et al. Hao describes several examples having useful afterglows of more than ten hours, whereas zinc sulphide materials are never as bright, and are almost extinguished at one hour. Moriyama et al (US 5770111) describe a modified phosphor with improved afterglow; in this phosphor a part of the strontium is substituted by at least one of Pb, Dy, and Zn.

There are a number of commercial and entertainment type applications for enhanced luminescent materials and this application relates in particular to materials made of a latex composition. Latex-based or rubbery items for which usual usefulness can be enhanced by building in an "afterglow" or "glow in the dark" capability include paints, inks, floormats, doormats, staircase treads, door handles, automobile and other control fascias, emergency exit signs and exit guides, and the like. DIN Standard 67510 and IMO resolution A.752(18) apply to photoluminescent safety markings.

Balloons have been a plaything for many years, and have uses such as in meteorology, for

aviators, or as part of a distinctive self-lifting sign. US5018532 Etheredge describes a phosphorescent condom, as does Kanai H (JP08215231) though Kanai specifies that the pigment lies between one latex layer and another. Kanai JP08243262 is for a balloon wherein the latex wall has a luminous paint mixed in with it. Lovik (US 4884990) describes a latex balloon, for which an inner layer of latex is filled with a ZnS type of phosphor and a second, outer layer of clear latex is superimposed. Nakamura (JP 05220274) describes a balloon bearing a scene, wherein a luminous paint and optionally an ordinary printing paint are used on the balloon to create the scene but the English-language abridgement gives no details of the paints used A 1992 filing date indicates it precedes the use of strontium aluminate.

DEFINITIONS

The term "**luminescent**" in relation to a material describes a property of giving off light over a period (perceptible to a human as being an extended period) after being illuminated. "Luminescent" is effectively synonymous with "phosphorescent". In contrast, "**fluorescent**" materials give off light (also of a longer wavelength) immediately on being illuminated. A "**phosphor**" is a chemical substance in which this property actually resides.

OBJECT

It is an object of this invention to provide a luminescent latex material and/or products including or carrying such a material, or at least to provide the public with a useful choice.

STATEMENT OF INVENTION

In a first broad aspect the invention provides a phosphor for inclusion in a coagulable medium in order to create an article which is capable of exhibiting luminescence, wherein the phosphor is selected from a group including an activated strontium aluminate and the phosphor is coated with an inert coating so that the phosphor is isolated from contact with the medium and is thereby prevented from reacting with one or more components of the medium.

In a related aspect this invention provides a luminescent substance comprising a plurality of granules or particles of luminescent material or phosphor; each particle having a coating capable of isolating the phosphor from an external environment.

Preferably the coating is optically and chemically inert.

In a further related aspect the invention provides an inert coating material suitable for providing an inert coating over particles of phosphor as previously described in this section, the material comprising a substantially transparent, fusible material, substantially insoluble in water and

non-reactive with the phosphor, the material being selected from the range of resins, plastics, and waxes.

Optionally the luminescent material is comprised of an alkaline metal aluminate having one or more activators; an example material is a strontium aluminate sintered with boron and with one or more rare earth elements such as europium, reduced, cooled, and ground into a fine powder.

In a yet further aspect the invention provides a method for the manufacture of a coated phosphor as previously described in this section,wherein the method includes the steps of selecting a finely powdered coating material from the range of resins, plastics, and waxes, thoroughly mixing the phosphor and the coating material under conditions which render the coating material at least partially fluid, solidifying the mixture and breaking it down to a fine powder in which the phosphor is substantially protected by a coating.

In another related aspect the invention provides an article composed at least partially of a luminescent latex, wherein the composition of the article includes a coated phosphor as previously described in this section, mixed with the latex prior to coagulation, so that the inert coating prevents interference with the process of coagulation.

Preferably the composition of the latex article includes from 10 to 85% by weight of a coated phosphor as previously described in this section.

More preferably the composition of the latex article includes from 20 to 40% by weight of a coated phosphor as previously described in this section.

In a still yet further related aspect the invention provides an ink suitable for printing on to a latex article, wherein the composition of the ink includes a suspension of a phosphor as previously described in this section, and a solution of rubber in a compatible solvent.

Preferably the composition of the ink includes a suspension of a phosphor, as previously described in this section, at up to 80% by weight, a rubber such as smoke sheet, and a compatible solvent.

In a yet still further related aspect the invention provides an at least partially luminescent latex-based article, wherein at least a portion of the article printed with an ink containing a coated phosphor as previously described in this section, so that the printed portion is capable of exhibiting luminescence.

In a second broad aspect the invention provides a method for printing markings on to a latex article, the method including the steps of stretching the latex article to an extent exceeding the

amount it would be stretched during use, printing with an ink as previously described in this section, hardening the ink, and allowing the article to revert to a contracted state.

In a related aspect the invention provides a method as previously described in this section, wherein the liquid material including a phosphor is maintained in a recirculating chamber prior to application, so that the components of the liquid remain in suspension.

In a third broad aspect this invention provides a luminescent substance comprising a composition based on a liquid capable of conversion into a resilient material, including an effective amount of a compatible luminescent material as previously described in this section.

A preferred liquid is a liquid latex, which can be dried against a surface into rubber.

Preferably the effective amount of a compatible luminescent material described previously in this section is between about 5 and about 40% by weight.

Preferably the luminescent material emits light having a predominant colour lying in a selected portion of the visual spectrum.

Optionally the luminescent material may comprise a mixture of materials each having a single emissive colour so that other colours may be produced. Optionally fluorescent materials capable of emitting a visible light may be included.

Optionally the luminescent material may also include coloured absorbent materials so that other colours may be produced.

In a fourth broad aspect this invention provides an object made at least in part from a latex composition as previously described in this section.

A preferred example object is a balloon comprised of the composition.

Another preferred example object is a balloon partially comprised of the composition and partially comprised of a non-luminescent latex.

A further preferred example object is a balloon comprised of the composition and bearing one or more indicia on at least one surface.

Yet another preferred example object is a balloon comprised of a non-luminescent latex and bearing one or more indicia made of a composition as previously described in this section on at least one surface.

An even further preferred example object is a balloon comprised at least in part of the composition and having a wall thickness of variable yet controlled thickness.

Preferably the variable thickness is initially applied to an inner surface of a balloon and preferably this is done by casting or forming the balloon over a mandrel having impressions on its surface, and optionally the balloon is later inverted.

Optionally a coating, comprised of a composition as previously described in this section, is then applied over the inverted balloon.

Optionally a coating having a protective function is applied over the inverted balloon.

A yet further preferred example object is a balloon having an internally applied detail produced by a method including the steps of applying removable indicia to a surface of a mandrel, covering the mandrel with a latex composition and causing the composition to dry.

Optionally the internally applied indicia is composed of a luminescent ink, or alternatively a non-luminescent ink.

In a fifth broad aspect the invention provides a method for making an object having resilience and luminescent properties, the method including the step of using a phosphor-containing composition as previously described in this section as a substitute for known methods for making similar objects not having the luminescent properties.

In a sixth broad aspect this invention provides a latex paint made at least in part from a composition as previously described in this section.

In a seventh broad aspect this invention provides a method for screen-printing markings on to a latex article, the method including at least one of the following steps: use of a relatively low screen mesh count of from about 86 to about 125 threads per inch, use of a relatively high screen tension, moderate squeegee and flood screen speeds, and consistent squeegee and flood screen pressures, use of over-printing with several layers of ink, use of an ink having between about 40% by weight and 80% by weight of phosphor, use of a recirculating pump for maintaining the phosphor in suspension within a recirculating chamber, use of overstretching the surface to be printed, before applying the ink, and use of frequent quality-assurance tests of luminosity.

PREFERRED EMBODIMENT

The description of the invention to be provided herein is/are given purely by way of example and are not to be taken in any way as limiting the scope or extent of the invention.

DRAWINGS

Fig 1: shows detail of a cross-section of a balloon, embodying several ways of using

a latex/phosphor combination according to the invention.

Fig 2: shows an embossed balloon according to the invention.

Fig 3: shows a method for printing onto a mandrel for making marked balloons according to the invention.

EXAMPLE 1

The coated phosphor itself is, in these examples, a strontium aluminate base including various activators such as europium (or other rare earths) and boron, as described in the prior art. These phosphors are significantly brighter than zinc sulphide, and continue to give out light for a much longer time after activation although a longer "charging" period is noted. Colours other than the usual green are also possible. Of course the invention is not to be read as being limited to these strontium-type phosphors. For instance, the significantly faster time course of a zinc sulphide phosphor in commencing release of light when illuminated may justify the inclusion of a proportion of this phosphor in a mixture.

As a result of (a) the invention of improved phosphors, and (b) effective ways to use them with latex, satisfactory "glow in the dark" balloons can be made - to give one example application of the invention. That is, enough light comes from a unit area of a distended balloon to create a suitable impression in a viewer's mind, whereas prior-art zinc sulphide phosphors were not very effective at all. If a balloon increases its diameter by ten times, the amount of active phosphor per unit area is reduced by 100 times. Hence balloon manufacture is a relatively demanding type of application for strontium-based phosphors.

The problem to be solved is that there have been substantial difficulties in making a luminous latex with these phosphors. Latex (which is an alkaline suspension, based on a sap from usually a rubber tree) is adversely affected by chemical effects from the phosphor which tend to make it form bubbles and refuse to coagulate. (This is despite claims by pigment manufacturers that the product is chemically and biologically inert). When one tries to make thick suspensions of phosphor for effective and dramatic effects, the lack of ability to coagulate frustrates the manufacturing process. **Our solution is** that we have found that a procedure of coating the individual grains of phosphor so that they are protected from the surrounding liquid, is effective.

Phosphors so treated have been found to be stable and in all other ways usable when mixed with aqueous latex suspensions. The preferred proportions depend somewhat on commercial considerations and ultimately on the stability of a blown-up balloon as well as on the effectiveness of luminescence desired, but are generally in the 5% to 45% by weight range, sometimes even up to 80%.

EXAMPLES OF COMPOSITIONS.

EXAMPLE 1.

This example is a coated phosphor, wherein the phosphor is preferably of the strontium aluminate family and the coating is capable of rendering the phosphor compatible with a suspension of latex (or the like) by sealing each granule of the phosphor from the aqueous latex. A suitable coating material is for example a resin of the type used in manufacturing toner materials for use in laser printers, or copier, although low melting point specifications are unnecessary for this application. A resin coating process similar to that used in making toner may be used. (The term "resin" refers generally (but not exclusively) to a plastics material. Styrene and acrylic resins, polyurethane resins, polyacylammonia resins, amino resins, poly vinyl alcohol resins, butyl aldehyde resins, and waxes may be used, also fluorine type resins or silicon type resins). Either acrylic or polyester resins are normally used.

For preparation of a coated phosphor according to the present invention, a high concentration of strontium aluminate phosphor ,powdered and having typically a mean particle size of 2 to 20 microns (μm), a resin composition selected from the above range, and optionally a pigment, a fluorophor, or dye (to serve as a colorant) are well blended together by a stirrer at a high speed. We prefer to use plastic mixing stirrers to avoid damage to the crystal structure of the phosphor. After pouring the resin on to a surface to solidify it (for convenience) as a sheet, breaking it up, grinding and sieving, a coated phosphor with an average particle size of from 1 to 70 microns (μm) (more preferably 3 to 20 μm) is obtained. Substantially all the phosphor is now isolated from contact with aqueous media. Optional types of coating include a relatively high melting-point paraffin wax or a styrene-based plastic material for the coating.

EXAMPLE 2.

For use of the phosphor with a paint or ink according to the present invention, a variety of transparent resins/binders may be used. Preferred binders are neutral or alkaline, transparent, and water clear. Heavy metal additives are contraindicated. Styrene and acrylic resins, polyure-

thane resins, polyacylammonia resins, amino resins, poly vinyl alcohol resins, butyl aldehyde resins, are acceptable. A selected resin or mixture of resins is mixed with a solvent, the luminous phosphor is added, and additives such as an anti-deposition agent, an erasing foam agent, and a dispersion agent are blended by a stirrer at a high speed. Preferably plastic mixing stirrers are used, to avoid damage to the crystal structure of the phosphor. If a sand grinder is used, the milling time should be as short as possible and simply disperse the phosphor.

Note that the binder and the phosphor should not be mixed until they are ready to be used. I believe that the mixture in its present form will keep for only about 2 hours, but this depends on specific resins. (Keeping is affected by (for example) eventual solubility of the coating in the solvent). A white primer coat may be applied beneath the mixture on to a surface, in order to enhance the resulting brightness.

EXAMPLE 3.

A latex composition including an effective amount (from 5% to 80%) of a coated phosphor as described in example 1 is suitable for the formation of resilient objects by causing the latex to dry and coagulate. This composition may comprise a stable suspension, but may require stirring before use. Optionally dyes, opacifiers, and the like may also be added although in general the addition of light-absorbing material detracts from the visual effect of the phosphor.

There is the possibility of (for example) using a red-emitting fluorescent phosphor in close contact with a green to blue (or violet or ultraviolet) emitting luminescent phosphor, so that the resulting light output is a combination of luminescent and stimulated fluorescence. In relation to this invention, the fluorescent phosphor may be included in the resin surrounding the strontium aluminate granules.

EXAMPLE 4.

A latex composition suitable for use as an ink on a latex balloon or the like. Optionally this mixture may also include optically active dyes or pigments. A preferred mixture comprises 30.7% of "smoke sheet" grade rubber, 24.8% solvent, "Super Lacolene" which is a light naphtha, and 44.5% of phosphor. One or more further additives (such as thixotropic agents or wetting agents) may be added in order to make the ink adhere better.

EXAMPLE 5.

A latex composition suitable for use as an ink on a microfoil balloon or the like. Optionally this mixture may also include optically active dyes or pigments, and additional compounds to promote adhesion. A preferred mixture comprises 48.7% of "Nazdar 7200 Lacquer", 12% "Barsol" solvent, and 39.3% of phosphor.

EXAMPLES OF PROCESSES.

The Internet web site of Latex Engineering BV (www.latexengineering.nl) as read on 24 June 1999 and 20 June 2000 provides a generic list of prior-art process steps for making a latex balloon and is hereby imported by way of reference.

EXAMPLE 1.

A self-luminous balloon - whether of conventional "drop" shape or some more elaborate shape - is preferably made by the usual technique, involving formation by dipping a suitably shaped mandrel one or more times into a latex composition including coated phosphors according to the invention, drying the coated mandrel, then stripping the balloon from the mandrel as is known in the art. Preferably the latex composition is continually stirred and a preferred means involves setting up a recirculating stream for each container, taking material from the bottom of the container through a pump, and returning it back near to the top of the container, preferably without mixing too much air into the liquid. The use of coated phosphors in the latex allows otherwise ordinary processing. Fig 1(a) shows at 100 a portion of a wall of a balloon of this type.

EXAMPLE 2.

A partially luminous balloon - whether of conventional "drop" shape or some more elaborate shape - is made by the usual technique involving formation by dipping a suitably shaped mandrel into a plain latex, drying the coated mandrel, then stripping the balloon from the mandrel. The balloon may then partially coated, or may be imprinted with indicia, patterns, or the like using a latex composition including coated phosphors according to the invention as an ink or paint. Fig 1(b) shows at 102 a portion of a balloon wall where a plain latex wall has an outer layer of luminous material attached. The ink or paint may optionally include conventional dyes or pigments, and fig 1 (c) illustrates a luminous wall balloon with a light-absorbing ink on top. Optionally the plain latex may include an inactive powder or opacifier having an appearance similar to that of the dried ink so that the imprinted indicia do not become visible until excited by the usual means. Alternatively the balloon may be made with a phosphor having a first luminescent colour (as in example 1) and the imprint may be in one or more other luminescent colours. (Many other variations will be evident to a reader skilled in the art).

Drying may be encouraged by means of dry air, heated air, or the like as is known in the art.

EXAMPLE 3.

An alternative process,"inside-out printing", involves a suitably shaped mandrel (see fig 3 - 301) which has temporarily held indicia 302 (inked areas) laid down onto its surface prior to being dipped into a latex. After stripping the balloon 303 from the mandrel and drying it as is known in the art, the balloon can be inverted again so that the indicia 305 are on the outside of the finished balloon 300. The step of laying down indicia on a mandrel resembles part of an offset printing process, although the transfer plate in this instance is a non-flat surface. The indicia or the latex may be luminous. This procedure should result in relatively permanent indicia. Of course it may be used with preparation of flat sheets as well - see example 7.

EXAMPLE 4.

A more conventional printing method developed for latex balloons in particular involves several strategies aimed at enhancing the ultimate effect of the phosphor. One or more of the strategies may be used in any instance. A screen-printing process is particularly considered.

Strategy 1. A screen mesh count of only about 86 to 125 threads per inch is used, because of the coarser particle size.

Strategy 2. Use high screen tension, moderate squeegee and flood screen speeds, and consistent squeegee and flood screen pressures, to deposit a thick layer.

Strategy 3. Over-print so that several layers of ink are built up. This dramatically increases the resulting brightness.

Strategy 4. Although usual screen-printing inks contain only about 30% pigment, it is preferable to use 40% and up to 80% phosphor. As described above, a recirculating pump is highly desirable in order to maintain the phosphor in suspension.

Strategy 5. Stretch the surface to be printed, perhaps to even twice the "design" stretch for which the balloon is intended, then print and after drying has occurred, allow the surface to retract.

Strategy 6. Test samples of the product in a darkened room by measuring the acquisition of luminosity and the rate of decay after exposure to a test source of light, having a known intensity and a known proportion of short wavelengths, for a set period. For example, use a fluorescent light for 5 minutes. Comparison of test samples with a standard sample simplifies this process. In the event of weak light output, investigate the cause and fix it.

EXAMPLE 5.

An embossed balloon surface can be formed as follows, so that quite detailed shaping of the surface can be created. See Fig 2. This alternative process involves detailing the mandrel surface, perhaps using spark erosion or chemical etching so that the mandrel surface bears the inverse of the desired surface. Printing as described in the previous example may also be applied. Then, when the mandrel is dipped into a latex (which may be a composition according to the invention) and after removal is dried, the balloon surface bears on the inside (see 200) finely detailed thickening (201) and thinning (202) according to the design used. After stripping the balloon from the mandrel and drying, the balloon can be turned inside out so that the surface details are on the outside (204). The balloon may then be dipped in or printer with a further latex solution 203 optionally when slightly distended, in order to cover the "valleys" of the surface. By way of illustration, a "Glow-in-the-dark Moon Balloon" can be made in this way. Detail (corresponding to the actual mountains, rills, craters, highlands, and the like can be impressed on the mandrel. The basic balloon may be made of yellow or green luminescent latex according to the invention. The second dipping may be in a grey pigmented latex 205 in order to create a brightness contrast that reveals the relief of the now outer surface, and optionally the lunar maria may be printed on with a light-absorbing ink 207. Optionally, a further latex layer 205 may then be added in order to act as a protective surface. Of course a similar through inferior version of a moon balloon may be made by simply printing a basic "Glow-in-the-dark balloon" with a pigmented latex ink.

EXAMPLE 6.

A resilient, luminescent sheet material is made by the usual technique involving drying a layer of liquid composition spread onto a flat or cylindrical surface, then stripping the polymerised layer from the surface and optionally shaping the surface to a desired outline. Drying may be encouraged by means of dry air, heated air, or the like as is known in the art. Example applications are in making temporary signs for crowd control at night events, or clothing for use by police or ambulance personnel at night. If a hand-shaped mould is used, luminous surgical gloves may be made and these are particularly useful for carrying out first aid in the dark.

EXAMPLE 7.

A resilient sheet material such as a bandage for use in emergency dark areas (such as a coal mine) is made by the usual technique involving drying the a layer of liquid composition spread onto a flat or cylindrical surface, then stripping the polymerised layer from the surface and optionally shaping the surface to a desired outline. Drying may be encouraged by means of dry air, heated air, or the like as is known in the art. Usefully, printed indicia such as directions for

use or expiry dates (such as for bandages) may be printed onto the material using preferably an ink or paint according to the invention. This example also relates to the production of flexible, resilient signage for use in emergency lighting situations, in buildings or the like, on apparel, or on domestic animals to be located in the dark.

EXAMPLE 8.

A resilient, luminescent three-dimensional shape is made by the usual technique involving drying the liquid composition after it is poured into a mould, then stripping the dried object from the mould. A process analogous to "slip casting" from pottery may be used. Drying may be encouraged by means of dry air, heated air, or the like as is known in the art. Note that luminescent or "glow in the dark" body costumes for humans to wear may be made by a similar process on a suitably shaped former.

EXAMPLE 9

A luminescent mixture may be sprayed or air-brushed on to a surface, preferably with directional control.

EXAMPLE 10

Printing onto a hard surface such as a ceramic or glassware involves use of a recipe comprising mixing of Medium 63/634 and phosphor in the ratio of 1 to 8, and adding about 20% by weight of a flux to the mixture. The flux is selected from the range of C1000 for a ceramic flux, Bell flux for glassware, and for direct press printing on to a thermoplastic substrate, VG23901. The flux tends to slightly colour the final result and this can be made an advantage. As before, a decreased screen mesh size, and multiple printing passes result in more phosphor per unit area and hence a brighter result.

In summary, a number of practical recipes have been provided in these Examples.

VARIATIONS

1. Note that references made to balloons in the preceding text can generally also be applied to condoms and other rubber-based devices.

2. While the invention may be considered to specify improved families of phosphors, such as those of US 5885483 involving variously activated strontium aluminates, it must be realised that further improvements to phosphors may be made resulting in further chemical families of phosphor, and the invention may then be applied to those. Nor is the invention solely limited to latex as described herein. Suspensions of coated phosphors in other liquids may have other commercial applications, such as in making paper (useful for taking down notes

in the dark), in paints, and the like. Indeed, the relatively non-toxic nature of these phosphors particularly when coated may permit their addition to novelty foods or drinks.

3. Electroluminescence is the emission of light as a result of exposure of certain luminescent materials to a changing electric field. Electroluminescent panels commonly are constructed with a capacitor structure using transparent or translucent electrodes and a phosphor within the dielectric. It may be possible to excite a polymerised latex composition including a coated phosphor according to the invention using suitably energised electrodes laid down in a controlled manner, and provide an electrically powered flexible light source, or an information display akin to liquid crystal displays, while making use of the coated phosphor. Possibly a different chemical composition of phosphor will be appropriate for use in electroluminescence, and possibly a non-aqueous medium will be required rather than latex, which retains a certain amount of water. For example a silicone or other resin might be used. Advantages of electroluminescence include the inherent brightness of the phosphor and extended release of the light after perhaps inadvertent termination of the power.

COMMERCIAL BENEFITS or ADVANTAGES

The invention makes possible the use of (a) improved families of phosphors, such as those of US 5885483 involving alkaline metal aluminates with selected activators, in combination with (b) latex type materials thereby enabling the production of products such as "glow-in-the-dark" balloons. Hitherto these were ineffective using traditional activated zinc sulphide phosphors, and hitherto the improved phosphors were incompatible with aqueous latex.

Furthermore, either the known phosphors or others not yet known may be toxic. The use of phosphor grains coated with an indigestible material (which is a usual characteristic of a resin or a wax) will go a long way towards reducing health risks associated with and possible ingestion of phosphors.

Although a number of preferred examples as described above have been disclosed for illustrative purposes, these disclosures are in no way to be considered as limiting examples. Those skilled in the art will appreciate that various modifications, additions, and substitutions are possible without departing from the scope and spirit of the invention as set forth in the following claims.

We claim:

1. A powdered phosphor for inclusion in a medium in order to create from the medium an article which is capable of exhibiting luminescence, characterised in that the phosphor is selected from a group including activated strontium aluminate and the phosphor is coated with an inert coating so that the phosphor is isolated from contact with the medium and is thereby prevented from reacting with one or more components of the medium, so that the medium is capable of being coagulated.

2. A luminescent article having a latex base, characterised in that the composition of the article includes a latex, and a coated phosphor as claimed in claim 1, mixed prior to coagulation of the latex, so that the inert coating prevents interference with the process of coagulation.

3. A luminescent article having a latex base, characterised in that the composition of the article includes from 10 to 85% by weight of a coated phosphor as claimed in claim 1.

4. A luminescent article having a latex base, characterised in that the composition of the latex article includes from 20 to 40% by weight of a coated phosphor as claimed in claim 1.

5. The use in the manufacture of a coated phosphor as claimed in claim 1, of an inert coating material, substantially insoluble in water and non-reactive with the phosphor, selected from the range of resins, plastics, and waxes.

6. A method for manufacture of a coated phosphor as claimed in claim 1, characterised in that the method includes the steps of selecting a finely powdered coating material from the range of resins, plastics, and waxes, thoroughly mixing the phosphor and the coating material under conditions which render the coating material at least partially fluid, solidifying the mixture and breaking it down to a fine powder in which the phosphor is substantially protected by a coating.

7. An ink suitable for printing on to a latex article, characterised in that the composition of the ink includes a suspension of a coated phosphor as claimed in claim 1, and a solution of rubber in a compatible solvent.

8. An at least partially luminescent latex-based article, characterised in that at least a portion of the article is printed with an ink containing a coated phosphor as claimed in claim 1, so that the printed portion is capable of exhibiting luminescence.

9. A method for printing markings on to a latex article, the method including the steps of stretching the latex article to an extent exceeding the amount it would be stretched during use, printing with an ink as claimed in claim 6, hardening the ink, and allowing the article to revert to a contracted state.

10. A method for screen-printing markings on to a latex article, the method including at least one of the following steps:

a) use of a relatively low screen mesh count of from about 86 to about 125 threads per inch,

b) use of a relatively high screen tension, moderate squeegee and flood screen speeds, and consistent squeegee and flood screen pressures,

c) use of over-printing with several layers of ink,

d) use of an ink having between about 40% by weight and 80% by weight of phosphor,

e) use of a recirculating pump for maintaining the phosphor in suspension within a recirculating chamber,

f) use of overstretching the surface to be printed, before applying the ink, and

g) use of frequent quality-assurance tests of luminosity.

1/2

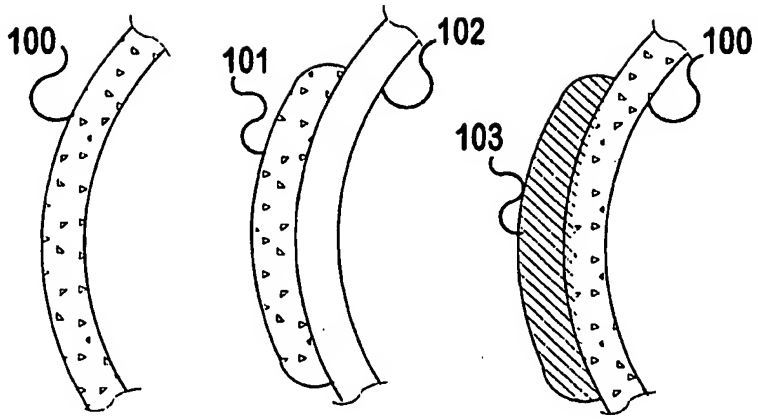
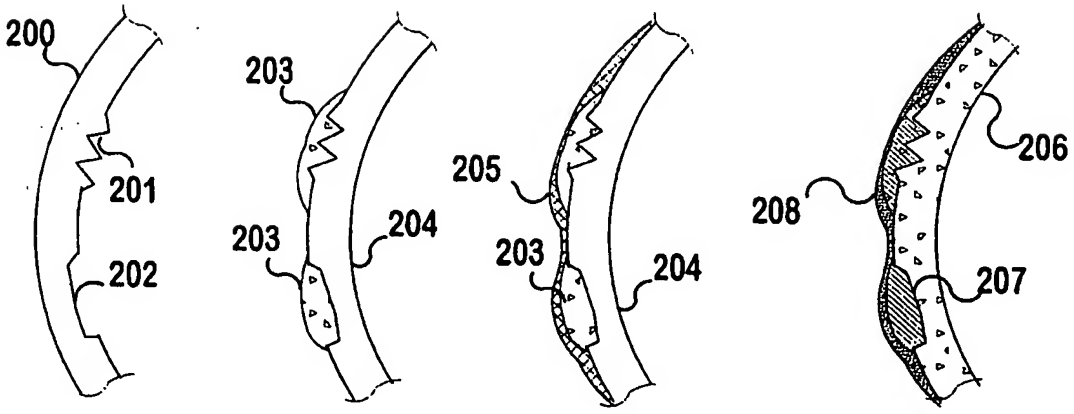

100
101
102
103
100
a
b
c

Fig 1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205
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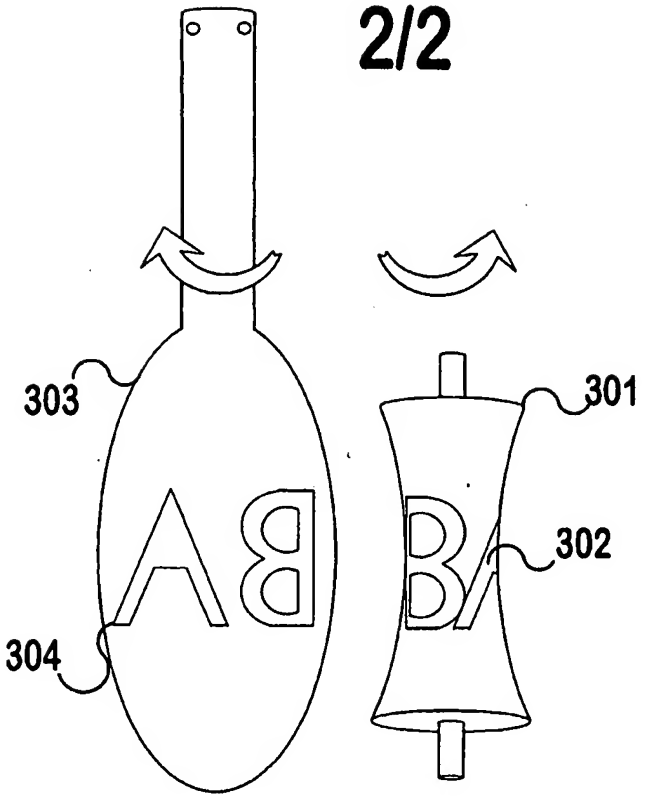
204
208
206
207
a
b
c
d

Fig 2



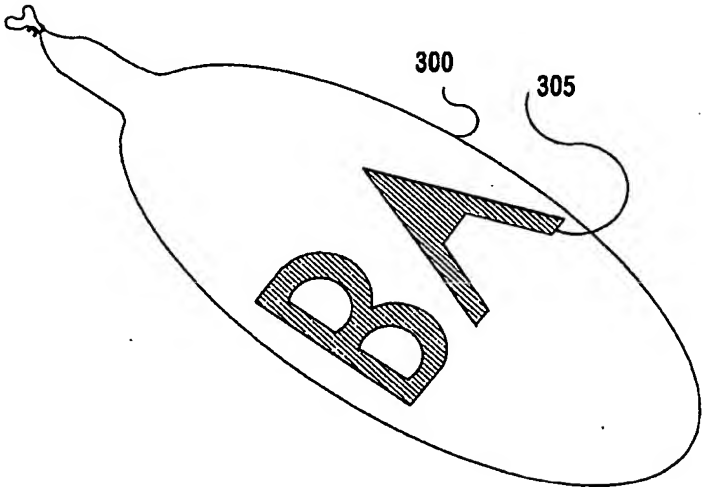


Fig 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ00/00108

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09K 11/02, 11/64; C09D 11/08, 5/22, 202/00; B41M 1/12, 1/32
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/301.4R, 301.36; 428/407; 101/129; 524/925, 575.5, 574; 523/ 161, 335, 334, 934; 427/157, 272, 275, 385.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 5,874,491 A (ANDERS) 23 February 1999, col. 2, lline 43-col. 10, line 42.	1,2,5,6 ---- 3,4
X ---- Y	US 5,665,793 A (ANDERS) 9 September 1997, col. 2, line 43-col. 8, line 63.	1,2,5,6 ---- 3,4
Y	US 4,902,929 A (TOYODA et al) 20 February 1990, col. 2, line 18-col. 8, line 29.	1,5,6
Y	US 3,961,106 A (HAYTMEIJER et al) 1 June 1976, col. 1, line 45-col. 6, line 33.	1,5,6
Y	US 4,884,990 A (LOVIK) 5 december 1989, col. 3, line 30-col. 12, line 11.	2-4

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 07 NOVEMBER 2000	Date of mailing of the international search report 08 DEC 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer C. MELISSA KOSLOW DEBORAH THOMAS PARALEGAL SPECIALIST Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ00/00108

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,854,306 A (MATTESKY et al) 29 December 1998, col. 1, line 28-col. 4, line 46.	6-10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ00/00108

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

252/301.4R, 301.36; 428/407; 101/129; 524/925, 575.5, 574; 523/ 161, 335, 334, 934; 427/157, 272, 275, 385.5